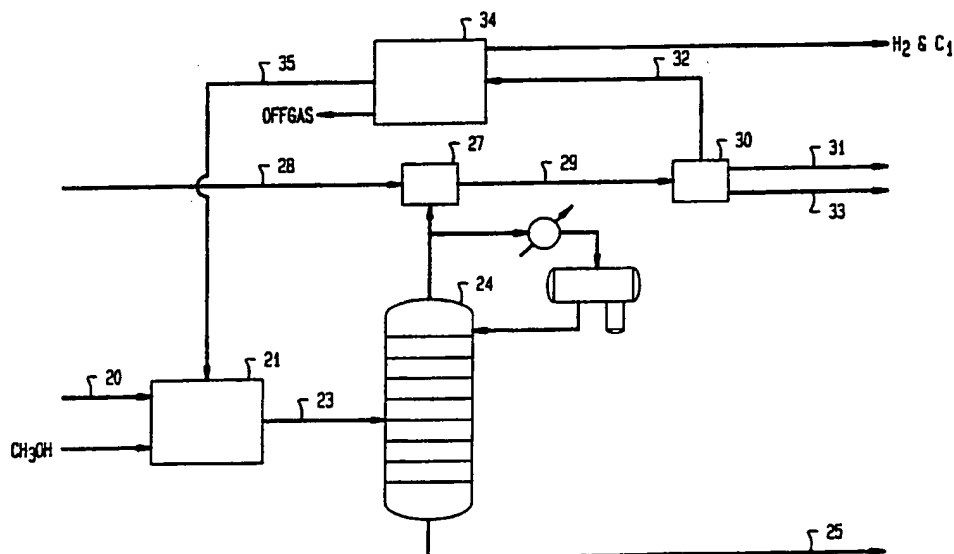




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(54) Title: OLEFINS ETHERIFICATION AND CONVERSION TO LIQUID FUELS WITH PARAFFINS DEHYDROGENATION



(57) Abstract

An integrated process for the production of ether-rich liquid fuels containing MTBE and TAME (25) by etherifying (21) a hydrocarbon feedstock containing C_4 + isoalkenes (20) in the presence of a stoichiometric excess of lower alkyl alcohol. Unreacted alcohol and olefins are passed to a zeolite catalysed conversion reactor (27) to produce gasoline (33) and light hydrocarbons (32). The light hydrocarbon fraction, comprising C_4 - C_5 paraffins (32), is dehydrogenated (34) and C_4 - C_5 olefins are recycled to the etherification reactor.

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OLEFINS ETHERIFICATION AND CONVERSION TO LIQUID FUELS
WITH PARAFFINS DEHYDROGENATION

This invention relates to processes for converting olefinic hydrocarbons to liquid fuels. In particular, this invention relates to a system for the production of methyl tertiary alkyl ethers combined with the conversion of olefins to gasoline and dehydrogenation of paraffins to olefins.

An important focus of current research into the production of high-octane gasoline is the blending of stocks with lower aliphatic alkyl ethers as octane boosters and supplementary fuels. C₅-C₇ methyl alkyl ethers, especially methyl tertiary butyl ether (MTBE) and tertiary amyl methyl ether (TAME), have been found particularly useful for enhancing gasoline octane.

It is known that isobutylene may be reacted with methanol over an acidic catalyst to provide MTBE and isoamylenes may be reacted with methanol over an acidic catalyst to product TAME. In these etherification processes a problem of major importance is that methanol is not totally converted. Separation of methanol from the etherification reaction product is made difficult by the tendency of methanol to form a very dilute azeotropic mixture with hydrocarbons, and by the strong solubility of methanol in both water and hydrocarbons. While it would be beneficial from an equilibrium standpoint to use large excesses of methanol in etherification these separation problems go against doing so. Due largely to these

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factors, the cost associated with conventional methanol separation and recycling in the etherification reaction represents approximately 30% of the cost of the total etherification process.

5 US-A-4,684,757 discloses that the well-known ability of zeolite type catalyst to convert methanol to olefins may be utilised by directing unreacted methanol from an etherification reaction to zeolite-catalysed conversion to olefin, thereby obviating the need to
10 separate and recycle methanol. US-A-3,960,978 and 4,021,502 disclose conversion of C₂-C₅ olefins, alone or in admixture with paraffinic components, into higher hydrocarbons over crystalline zeolites having controlled acidity. Reaction conditions of moderate severity favour
15 the conversion of olefins to predominantly gasoline boiling range products with little paraffins conversion. Milder reaction temperatures and high operating pressures can produce distillate range fuels as well from lower olefins. US-A-4,150,062, 4,211,640, 4,227,992, 3,931,349
20 and 4,404,414, and C.D. Chang, Catal. Rev.-Sci. Eng., 25, 1 (1983) describe processing techniques in this field which may employ methanol or olefins as feed.

It is an object of the present invention to provide an improved process for the production of high
25 octane gasoline incorporating methyl tertiaryalkyl ethers from isoalkene-rich hydrocarbons.

We have now discovered that high octane gasoline can be produced employing an improved etherification process that can utilise large stoichiometric excesses of
30 lower alcohols such as methanol. Optionally, C₃-hydrocarbons from the dehydrogenation step may be separated and passed to the olefins conversion zone containing metallosilicate catalyst such as zeolite ZSM-5.

According to the present invention a process for

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the preparation of ether-rich liquid fuels and olefinic gasoline comprises reacting a feed containing C₄+ iso-alkene and excess lower alcohol over an acidic etherification catalyst to a product stream containing C₅+ tertiary alkyl ether, separating said stream into ether-rich gasoline range hydrocarbons, unreacted alcohol and C₄- or C₅- hydrocarbons, converting unreacted alcohol and C₄-/C₅- hydrocarbons at elevated temperature in the presence of a catalyst comprising an intermediate-pore zeolite to a mixture of C₄-C₅ paraffins, C₃- hydrocarbons and light gases and a liquid product comprising C₆+ olefinic gasoline, converting said paraffins to C₄-C₅ olefins under dehydrogenation conditions and recycling said olefins for co-feeding with said C₄+ iso-alkene.

The preferred lower alcohol is methanol and the preferred ethers comprise C₅+ methyl tertiary alkyl ether. The feed may be contacted with the etherification catalyst in the liquid phase and may additionally comprise C₄-C₉ hydrocarbons and contain C₄-C₇ alkenes and C₅+ gasoline-range non-etherifiable aliphatic hydrocarbons. The separation following etherification can be effected by distillation.

The mixture resulting from contact with the zeolite catalyst is of higher average molecular weight than the feed to that zeolite catalyst and advantageously contains branched C₄-C₅ hydrocarbons. Its C₃-hydrocarbons may be recycled for co-feeding with said unreacted alcohol and C₄-/C₅- hydrocarbons.

Reverting to the etherification step, the product unreacted alcohol and C₄-/C₅- hydrocarbons may constitute an azeotropic mixture. The lower alcohol is suitably present in the feed to the etherification catalyst in 2 to 50 percent stoichiometric excess relative to C₄+ iso-alkene, preferably 3 to 33, more preferably 3

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to 10, percent excess. A component of that feed may comprise a mixture of butylene isomers, light olefinic naphtha and methanol. The ether rich gasoline range hydrocarbons advantageously comprise a mixture of MTBE, TAME and unreacted naphtha. The feed to the zeolite catalyst may comprise a mixture of unreacted methanol, paraffins and butylenes.

In a particularly favoured flowscheme the product stream from the etherification is separated by aqueous extraction and distillation of unreacted methanol, an overhead vapour stream from said distillation comprising a portion of said unreacted methanol and C₄-/C₅- hydrocarbons being fed to said zeolite catalyst, a bottom liquid stream from said distillation constituting said ether-rich gasoline, the remainder of said unreacted methanol forming part of a aqueous stream from which it is recovered and recycled for feeding to the etherification catalyst.

The etherification catalyst is suitably a sulfonic acid resin, and the reaction over it is conducted at 40 to 80°C. The zeolite is preferably one having a constraint index of 1 to 12, suitably ZSM-5 having a silica/alumina mole ratio of 25 to 80 and at least partly in the hydrogen form, and the conversion over it is advantageously conducted at a temperature of 204 to 500°C and a pressure of 420 to 2100 kPa.

The dehydrogenation may be catalytic, in which case a catalyst comprising a Group VIII metal is suitably employed, the dehydrogenation conditions comprising a temperature of 550 to 650°C and a pressure of 16.95 to 101.7 kPa.

From another aspect, the present invention comprises a process for the conversion of C₂+ hydrocarbons to ether-rich liquid fuels and high quality

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aliphatic/aromatic gasoline comprising:

- (a) reacting a fresh hydrocarbon stream containing C₄+ isoalkenes with an excess of methanol in an etherification zone in contact with an acidic etherification catalyst under etherification conditions whereby an effluent stream containing methyl tertiary alkyl ethers is produced;
- (b) separating said etherification effluent stream to provide a first stream comprising ether-rich gasoline range hydrocarbons and a second stream comprising unreacted methanol and C₄- or C₅- hydrocarbons;
- (c) contacting said second stream with an acidic metallocsilicate catalyst in a conversion zone under olefins oligomerisation conditions at elevated temperature;
- (d) separating said conversion zone olefins oligomerisation effluent stream into component streams comprising C₄-C₅ hydrocarbons, C₃ hydrocarbons and light gases, and C₅+ olefinic gasoline;
- (e) contacting said C₄-C₅ hydrocarbon stream with a dehydrogenation catalyst under dehydrogenation conditions whereby C₄-C₅ paraffins are converted to olefins;
- (f) separating the dehydrogenation effluent stream and passing the portion thereof comprising C₄+ olefins to said etherification zone in conjunction with said fresh hydrocarbon stream and methanol for conversion to methyl tertiaryalkyl ethers.

Figure 1 is a schematic drawing of the process flow diagram of an embodiment of the invention.

In the preferred embodiment of the invention the principal components of known processes are integrated in a manner providing a highly advantageous and surprising advancement in refinery technology leading to the

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production of high octane gasoline and distillate. Known processes are combined in a unique configuration that provides enhancement of the performance of component processes as well as achieving surprising advantages for the integrated process. The processes integrated include etherification to produce ethers such as MTBE and TAME, the conversion of alcohols such as methanol to gasoline (known as the MTG process) and the conversion of olefins to gasoline (known as the MOG process). The MTO and MOG processes are closely related processes, employing an intermediate pore (5 to 7 μ m) zeolite as catalyst, whose operating conditions are selected to shift the conversion reaction toward the production of olefins and the conversion of olefins to gasoline. The above processes are further integrated in a novel way through a dehydrogenation step to yield the fully integrated process of the invention.

The reaction of methanol with isobutylene and isoamylenes at moderate conditions with a resin catalyst is established technology, described by R.W. Reynolds, et al in The Oil and Gas Journal, June 16, 1975, S. Pecci and T. Floris in Hydrocarbon Processing, December 1977, and J.D. Chase, et al, in The Oil and Gas Journal, April 9, 1979, pages 149-152. A preferred catalyst is a bifunctional ion exchange resin which etherifies and isomerises the reactant streams. A typical acid catalyst is Amberlyst 15 sulfonic acid resin.

Processes for producing and recovering MTBE and other methyl tertiaryalkyl ethers from C₄-C₇ isolefins are disclosed in US-A-4,544,776 and 4,603,225. Suitable extraction and distillation techniques for recovering ether and hydrocarbon streams from etherification effluents are likewise well known in the art.

As hereinabove set forth, lower paraffins such

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as C₄-C₅ hydrocarbons from the zeolite-catalysed conversion step are separated and passed to a dehydrogenation zone for dehydrogenation to olefins. It has been established that the conversion of paraffins, such as propane and butane, to mono-olefins, such as propylene and butylene, can be accomplished by thermal or catalytic dehydrogenation. A general discussion of thermal dehydrogenation (i.e., steam cracking) is presented in Encyclopedia of Chemical Technology, Ed. by Kirk and Othmer, Vol. 19, 1982, Third Ed., pp 232-235. Various processes for catalytic dehydrogenation are available in the prior art, including the Houdry Catofin process of Air Products and Chemicals, Inc., Allentown, Pa., the Oleflex process of UOP, Inc., Des Moines, ILL. and the process disclosed in US-A-4,191,846. The Houdry Catofin process, described in "Dehydrogenation Links LPG to More Octane", Gussow et al, Oil and Gas Journal, Dec. 8, 1980, involves a fixed bed, multi-reactor catalytic process for conversion of paraffins to olefins. Typically, the process operates at pressures of 5-30 inches of mercury (16.95 to 101.7 kPa) absolute, and high temperatures with hot reactor effluent at 550-650°C. Dehydrogenation is an endothermic reaction, so it normally requires a furnace to provide heat to a feed stream prior to feeding the feed stream into the reactors. The UOP Oleflex process, disclosed in "C₂/C₅ Dehydrogenation Updated", Verrow et al, Hydrocarbon Processing, April 1982, uses stacked catalytic reactors. US-A-4,191,846 discloses the use of Group VIII metal containing catalysts to promote catalytic dehydrogenation of paraffins to olefins.

Referring now to Figure 1, etherification hydrocarbon feedstream 20 preferably comprises a C₄+ hydrocarbon stream rich in isoalkenes. The hydrocarbon

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stream is passed to etherification reactor 21 and mixed with at least 2% excess of methanol based on the isoalkene content of the hydrocarbon stream. A unique advantage of the present invention is the capability to use large stoichiometric excesses of methanol in the etherification reaction, thereby promoting the improved formation of ethers. Excess methanol in the range of 2 to 50% may be conveniently used. The etherification reaction is conducted at 40 to 80°C, preferably at about 60°C. The etherification effluent is passed 23 to a fractionator 24 wherein a bottom stream 25 is separated comprising ether-rich gasoline. The overhead from the fractionator comprises essentially etherification excess methanol and all or a major portion of unreacted hydrocarbon. The mixture is passed to an olefins to gasoline (MOG) conversion reactor 27 supplemented, optionally, by a feedstream 28 of C₃-olefinic hydrocarbons. Olefins are converted to gasoline at a pressure between 420 kPa and 2100 kPa (60 and 300 psia) and a temperature between 204 and 500°C. Under these conditions methanol in the mixture is also converted to higher hydrocarbons including C₄-C₅ olefins. The conversion effluent is passed 29 to a fractionation unit 30 for the separation of C₃-fuel gas 31, C₄-C₅ paraffins 32 and a C₅-C₉ gasoline product 33. The C₄-C₅ paraffins are passed to a dehydrogenation zone 34 where they are dehydrogenated to olefins. C₄-C₅ olefins are recovered from the dehydrogenation effluent stream 35 and passed to the etherification zone 21. Optionally a C₃-olefin stream may also be recovered from the dehydrogenation stream and recycled to the olefins to reactor 27. Alternatively, C₂-C₃ components leaving reactor 27 can be sent to the dehydrogenation unit for further conversion to olefins which can be upgraded in reactor 27. The dehydrogenation reactor effluent can be

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fed to the etherification unit without separating or efficiently separating C₃- components from C₄- components. This will allow utilising the MOG separation section as the only gas plant in the process.

5 According to an advantageous embodiment of the invention conventional etherification processes to produce MTBE, where the etherification reaction effluent stream is extracted with water to remove excess or unreacted methanol and unreacted methanol recovered by distillation
10 for recycle to the etherification reactor, are improved: the hydrocarbon portion of the effluent stream after aqueous extraction is separated into C₄+ hydrocarbon overhead stream containing unrecovered methanol for further conversion in contact with medium pore shape
15 selective catalyst followed by dehydrogenation of C₄-C₅ aliphatic hydrocarbons as described above.

 The catalyst employed according to the invention in the conversion of methanol and olefins is an intermediate-pore-size zeolite, most prominent among which
20 is zeolite ZSM-5. Such zeolites, which typically possess a constraint index of 1 to 12, are usually synthesised with Bronsted active sites by incorporating a tetrahedrally coordinated metal such as Al, Ga, B or Fe within the zeolitic framework. The advantages of ZSM-5
25 structures may be utilised by employing highly siliceous materials, such as those disclosed in CA-A-1,121,975, or crystalline metallocosilicate having one or more tetrahedral species having varying degrees of acidity. Zeolite ZSM-5 is defined by its x-ray diffraction data, set forth in US-
30 A-3,702,866. Other suitable zeolites include ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-34, ZSM-35, ZSM-38 and ZSM-48, defined respectively by the x-ray data set forth in US-A-3,709,979, 3,832,449, 4,076,979, 4,076,842, 4,016,245, 4,086,186, 4,046,859 and 4,375,573. Aluminosilicate forms

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of ZSM-5 of silica/alumina mole ratio 15 to 1600 may be employed, preferred catalysts comprising ZSM-5 of silica/alumina mole ratio 25 to 80, the zeolite being in the hydrogen form. Usually the zeolite will be employed
5 in the form of a composite with a refractory oxide matrix, such as alumina, silica and/or clay, of which the zeolite constitutes from 5 to 95, preferably 50 to 75, weight percent.

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CLAIMS

1. A process for the preparation of ether-rich liquid fuels and olefinic gasoline comprising reacting a feed containing C₄+ iso-alkene and excess lower alcohol over an acidic etherification catalyst to a product stream
5 containing C₅+ tertiary alkyl ether, separating said stream into ether-rich gasoline range hydrocarbons, unreacted alcohol and C₄- or C₅- hydrocarbons, converting unreacted alcohol and C₄-/C₅- hydrocarbons at elevated temperature in the presence of a catalyst comprising an
10 intermediate-pore zeolite to a mixture of C₄-C₅ paraffins, C₃- hydrocarbons and light gases and a liquid product comprising C₆+ olefinic gasoline, converting said paraffins to C₄-C₅ olefins under dehydrogenation conditions and recycling said olefins for co-feeding with
15 said C₄+ iso-alkene.

2. A process according to claim 1 wherein the lower alcohol is methanol and the ether comprises C₅+ methyl tertiary alkyl ether.

3. A process according to claim 1 or claim 2 wherein said feed is contacted with the etherification catalyst in the liquid phase.

4. A process according to any preceding claim wherein said feed comprises C₄-C₉ hydrocarbons and contains C₄-C₇ alkenes and C₅+ gasoline-range non-etherifiable aliphatic hydrocarbons.

5. A process according to any preceding claim wherein said separating is effected by distillation.

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6. A process according to any preceding claim wherein said mixture is of higher average molecular weight than the feed to said zeolite catalyst and contains branched C₄-C₅ hydrocarbons.

7. A process according to any preceding claim wherein said C₃- hydrocarbons are recycled for co-feeding with said unreacted alcohol and C₄-/C₅- hydrocarbons.

8. A process according to any preceding claim wherein said unreacted alcohol and C₄-/C₅- hydrocarbons constitute an azeotropic mixture.

9. A process according to any preceding claim wherein the lower alcohol is present in the feed to the etherification catalyst in 2 to 50 percent stoichiometric excess relative to C₄+ iso-alkene.

10. A process according to claim 9 wherein said excess is 3 to 33, preferably 3 to 10, percent.

11. A process according to any preceding claim wherein the feed to the etherification catalyst comprises a mixture of butylene isomers, light olefinic naphtha and methanol.

12. A process according to any preceding claim wherein the feed to the zeolite catalyst comprises a mixture of unreacted methanol, paraffins and butylenes.

13. A process according to any preceding claim wherein said ether rich gasoline range hydrocarbons comprise a mixture of MTBE, TAME and unreacted naphtha.

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14. A process according to any preceding claim wherein the product stream from the etherification is separated by aqueous extraction and distillation of unreacted methanol, an overhead vapour stream from said
5 distillation comprising a portion of said unreacted methanol and C₄-/C₅- hydrocarbons being fed to said zeolite catalyst, a bottom liquid stream from said distillation constituting said ether-rich gasoline, the remainder of said unreacted methanol forming part of a
10 aqueous stream from which it is recovered and recycled for feeding to the etherification catalyst.

15. A process according to any preceding claim wherein the etherification catalyst is a sulfonic acid resin.

16. A process according to any preceding claim wherein the reaction over the etherification catalyst is conducted at 40 to 80°C.

17. A process according to any preceding claim wherein the zeolite has a constraint index of 1 to 12.

18. A process according to any preceding claim wherein the zeolite is ZSM-5 having a silica/alumina mole ratio of 25 to 80.

19. A process according to any preceding claim wherein the zeolite is in the hydrogen form.

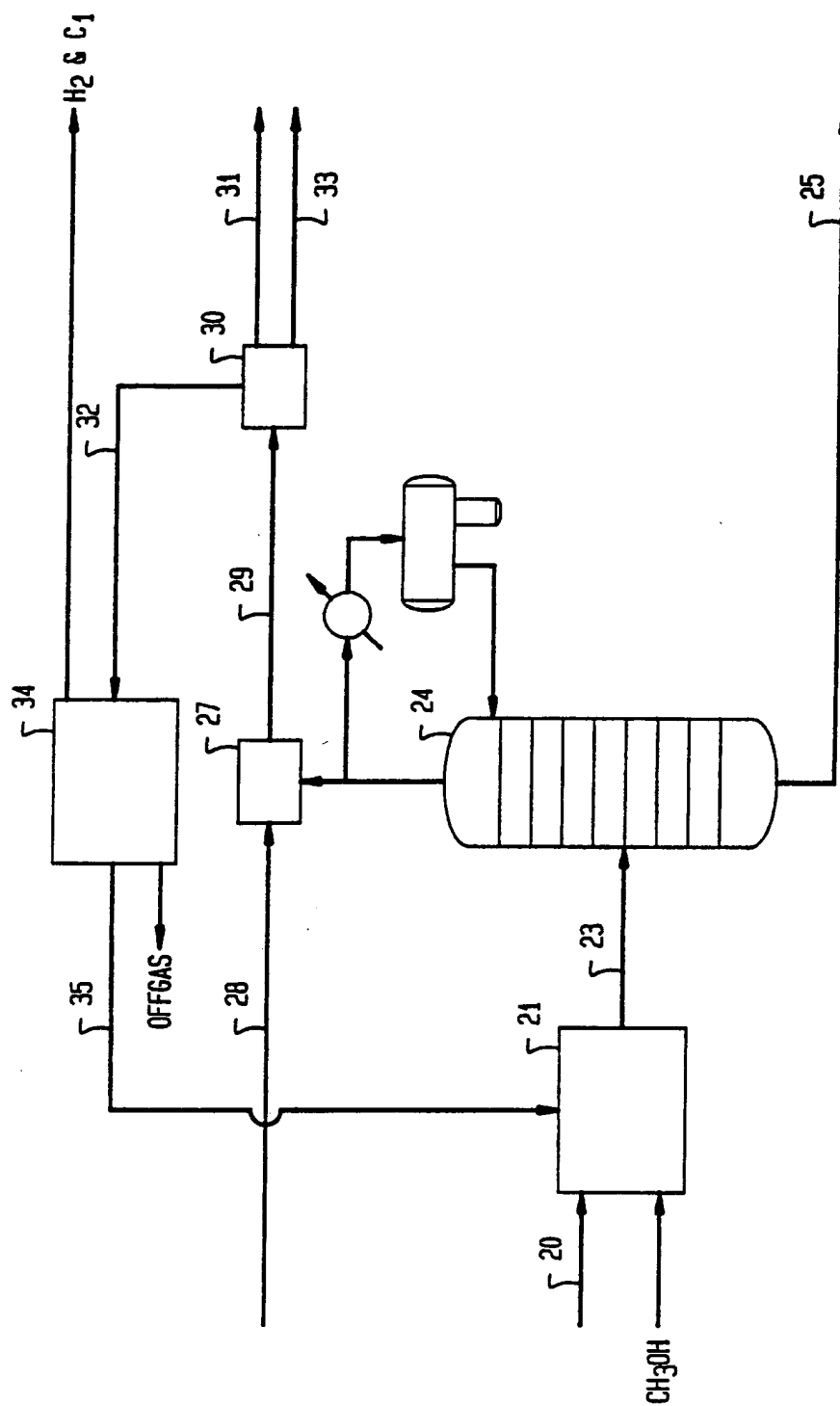
20. A process according to any preceding claim wherein the conversion in the presence of the zeolite catalyst is conducted at a temperature of 204 to 500°C and a pressure of 420 to 2100 kPa.

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21. A process according to any preceding claim wherein said dehydrogenation employs a catalyst comprising a Group VIII metal.

22. A process according to any preceding claim wherein said dehydrogenation conditions comprise a temperature of 550 to 650°C and a pressure of 16.95 to 101.7 kPa.

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SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/01287

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
INT. CL. ⁴ C10L 1/18		
US. CL. 44/53		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
US	44/53,77	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category [*]	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y, E	US, A, 4,830,635, (HARANDI ET AL) 16 MAY 1989, See entire document.	1-22
Y, E	US, A, 4,827,046, (HARANDI ET AL) 02 MAY 1989, See entire document.	1-22
Y, E	US, A, 4,826,507, (HARANDI ET AL) 02 MAY 1989, See entire document.	1-22
Y	US, A, 4,191,846, (FARAH, JR. ET AL) 04 MARCH 1980, See entire document.	1-22
A	US, A, 4,413,150, (BRIGGS) 01 NOVEMBER 1983, See entire document.	1-22
A	US, A, 4,252,541, (HERBSTMAN) 24 FEBRUARY 1981, See entire document.	1-22
A	US, A, 4,193,770, (CHASE ET AL) 18 MARCH 1980, See entire document.	1-22
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
07 JULY 1989		19 JUL 1989
International Searching Authority ISA/US		Signature of Authorized Officer ELLEN MCAVOY